

# Light-Driven Depolymerization of Native Lignin Enabled by Proton-Coupled Electron Transfer

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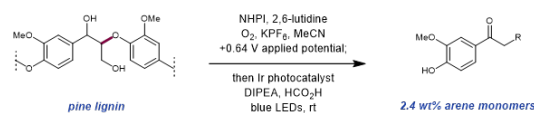
**ABSTRACT:** Here we report a catalytic, light-driven method for the redox-neutral depolymerization of native lignin biomass at ambient temperature. This transformation proceeds via a proton-coupled electron-transfer (PCET) activation of an alcohol O–H bond to generate a key alkoxy radical intermediate, which then facilitates the  $\beta$ -scission of a vicinal C–C bond. Notably, this single-step depolymerization is driven solely by visible-light irradiation, requires no stoichiometric chemical reagents and produces no stoichiometric waste. This method exhibits good efficiency and excellent selectivity for the activation and fragmentation of the  $\beta$ -O-4 linkage in the polymer backbone, even in the presence of numerous other PCET-active functional groups. The feasibility of this protocol in enabling the cleavage of the  $\beta$ -1 linkage in model lignin dimers was also demonstrated. These results provide further evidence that visible-light photocatalysis can serve as a viable method for the direct conversion of lignin biomass into valuable arene feedstocks.

**KEYWORDS:** lignin depolymerization, proton-coupled electron transfer, alkoxy radicals, C–C bond cleavage, photoredox catalysis

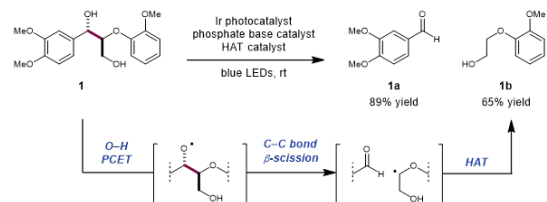
Lignin accounts for nearly 30% of the organic carbon on Earth, and is often proposed as a renewable alternative to petroleum for the production of aromatic feedstock chemicals.<sup>1</sup> However, the selective conversion of polymeric lignin into useful monomeric products is challenging due to its robust and complex structure, which is comprised of three structurally distinct cinnamyl alcohol subunits linked through strong C–O and C–C bonds.<sup>2</sup> Accordingly, traditional lignin valorization methods require harsh reaction conditions and high temperatures or pressures, as well as generating stoichiometric chemical waste streams.<sup>1a, 2-3</sup> As a consequence, these processes can suffer from poor product selectivity, product repolymerization, and challenges associated with product separation and purification. Hence, much current research is focused on the development of new chemical strategies for depolymerization that are highly selective and operate under mild conditions, allowing for the generation of well-defined product distributions.<sup>4</sup>

In this context, photocatalytic approaches to lignin valorization have begun to garner significant interest.<sup>5</sup> These reactions typically occur under milder conditions than conventional thermal reactions, and excited-state mechanisms can afford alternative cleavage products. A number of groups have recently developed novel strategies for lignin cleavage using both homogenous and heterogenous photocatalysts, including leading reports by Stephenson,<sup>6</sup> Soo,<sup>7</sup> Mariano<sup>8</sup> and Wang.<sup>9</sup> Despite this recent progress, many of these reports focus on the cleavage of model systems and small-molecule lignin fragments, and few have been adapted for use in the depolymerization of plant-derived polymeric lignin material. In a notable exception, Stephenson and co-workers recently developed a highly selective two-step depolymerization protocol for

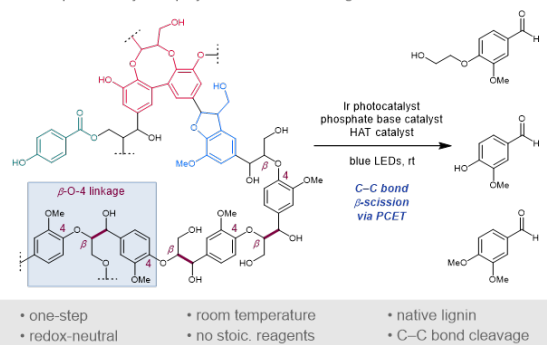
**A** Dual electrochemical/photoredox lignin depolymerization via C–O cleavage (Stephenson)



**B** Prior work: catalytic C–C bond cleavage reaction via PCET activation of alcohol O–H bonds



**C** This work: photocatalytic depolymerization of native lignin via PCET

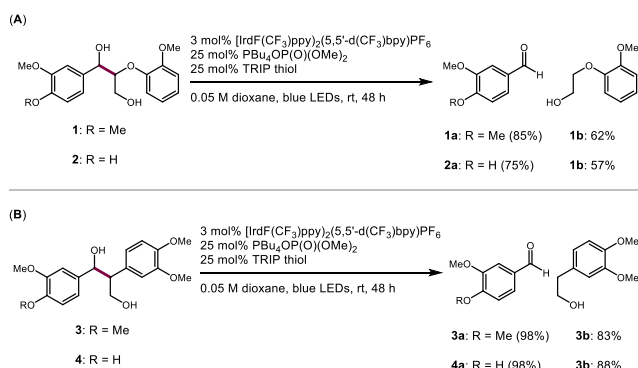


**Figure 1.** (a) Stephenson's photocatalytic lignin depolymerization. (b) C–C bond cleavage of a model lignin dimer via O–H PCET. (c) Photocatalytic depolymerization of native lignin via O–H PCET.

native lignin that operates at ambient temperature through rupture of the central C–O bond of the  $\beta$ -O-4 linkage, providing up to 2.4 wt% of monomeric arene products (Figure 1a).<sup>4h</sup> Complementary methods for photocatalytic

C–C bond cleavage in the valorization of unfunctionalized native lignin remain rare.

Our group has recently developed a number of photocatalytic methods for C–C bond functionalization based on the proton-coupled electron transfer (PCET) activation of the O–H bonds in simple aliphatic alcohols.<sup>10</sup> In these reactions, an excited-state oxidant and a weak Brønsted base jointly mediate the PCET oxidation of an alcohol substrate to furnish a reactive alkoxy radical intermediate that undergoes subsequent  $\beta$ -scission to cleave a vicinal C–C bond. We previously demonstrated that this method can be used to achieve the efficient fragmentation of model lignin dimer **1** to furnish aldehyde **1a** and alkoxyarene **1b** in good yields (Figure 1b).<sup>10b</sup> Zhang and co-workers recently adapted these PCET conditions for the depolymerization of *O*-methylated lignin.<sup>11</sup> Here, we demonstrate that an improved PCET protocol can also mediate the successful depolymerization of unfunctionalized native lignin (Figure 1c). These reactions are mediated by three distinct molecular catalysts—an Ir(III) chromophore, a dialkyl phosphate base, and an aryl thiol H-atom donor—that function together to selectively cleave the C–C bond of the lignin  $\beta$ -O-4 and  $\beta$ -1 linkages in a redox-neutral fashion. Notably, this process occurs near room temperature, requires no stoichiometric reagents, produces no stoichiometric waste, and consumes only photons. The development, optimization, and experimental implementation of the process are described herein.

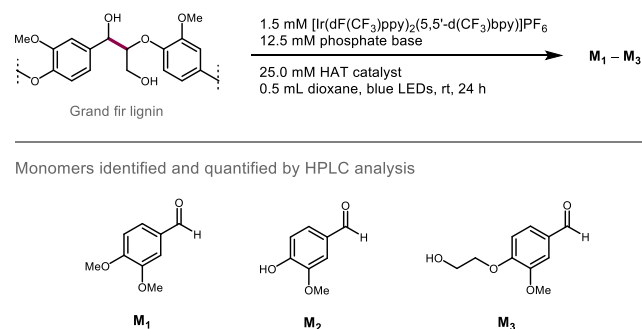


**Scheme 1.** (a) Catalytic C–C bond cleavage reactions of  $\beta$ -O-4 model lignin dimers. (b) Catalytic C–C bond cleavage reactions of  $\beta$ -1 model lignin dimers. All reactions were performed on 0.2 mmol scale. Yields were determined by <sup>1</sup>H-NMR analysis of the crude reaction mixtures relative to an internal standard.

In our previous report on the catalytic  $\beta$ -scission of aliphatic alcohols, we observed that model lignin dimer **1** underwent selective C–C bond cleavage at the  $\beta$ -O-4 linkage with high efficiency under the action of [Ir(dF(CF<sub>3</sub>)ppy)<sub>2</sub>(5,5'-d(CF<sub>3</sub>)bpy)]PF<sub>6</sub> (**Ir**), 2,4,6-triisopropylbenzene thiol (TRIP thiol), and tetrabutylphosphonium dimethylphosphate upon blue light irradiation to provide 3,4-dimethoxybenzaldehyde (**1a**) and (2-hydroxyethyl)guaiacol (**1b**) in 89% and 65% isolated yield, respectively.<sup>10b</sup> We expected that analogous reactivity in native lignin may prove more challenging due to the presence of endogenous phenols, which are excellent substrates for PCET activation themselves.<sup>12</sup> Given the large bond strength differential between phenol and aliphatic alcohol O–H bonds (BDFEs ~ 89 and 105 kcal/mol,

respectively),<sup>13</sup> we were concerned that phenol activation may occur preferentially and thus serve to poison the desired C–C bond cleavage reactivity. We were thus pleased to find that subsection of phenolic model compound **2** to the established cleavage conditions provided vanillin (**2a**) and **1b** in 47% and 36% yields, respectively. Changing the solvent from toluene to dioxane significantly improved the yields of **2a** and **1b** to 75% and 57% yield, respectively (Scheme 1a). We attribute the success of these reactions to the reversible PCET activation of O–H bonds. More specifically, we hypothesize that even if the weaker phenolic O–H bond is preferentially activated under our reaction conditions, if the resulting phenoxy radical does not undergo productive chemistry, it either abstracts a hydrogen atom from thiol or undergoes back electron transfer with the reduced state of the iridium photocatalyst to reform the substrate. By contrast, while PCET activation of benzylic O–H bond is thermodynamically less favored, the transient benzylic alkoxy radical triggers an irreversible C–C bond scission process, enabling the formation of the desired products. When applied to methoxy dimer **1**, the new conditions gave comparable results to those previously reported (i.e., 85% and 62% yield for **1a** and **1b**, respectively). Moreover, we observed that  $\beta$ -1 model lignin dimers **3** and **4** were also fragmented efficiently, providing the corresponding monomers in good yields (Scheme 1b).

**Table 1.** Optimization studies of the depolymerization reaction of native lignin.<sup>a</sup>



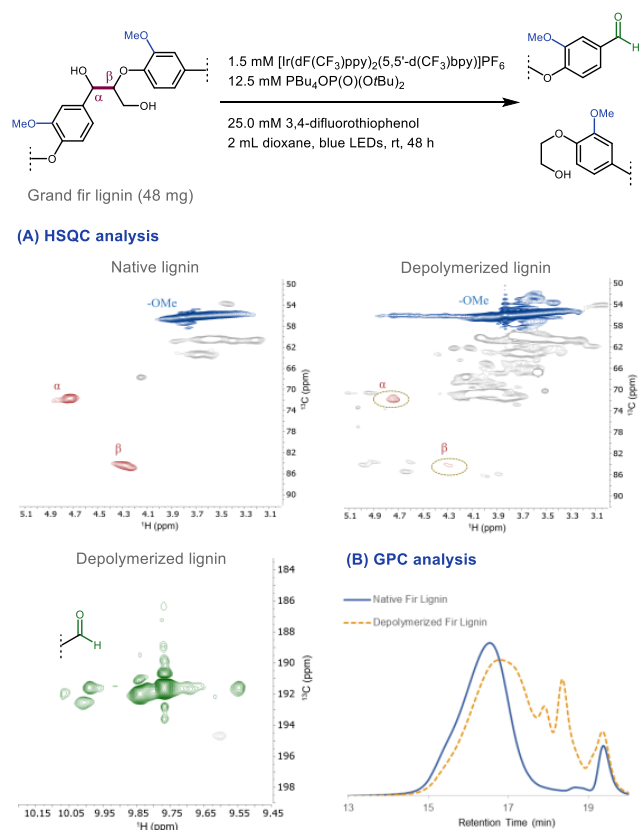
Entry	Phosphate base	HAT catalyst	M <sub>1</sub> (wt%)	M <sub>2</sub> (wt%)	M <sub>3</sub> (wt%)
1	PBu <sub>4</sub> OP(O)(OMe) <sub>2</sub>	TRIP thiol	0.3	0.3	0.3
2	PBu <sub>4</sub> OP(O)(O <sup>n</sup> Bu) <sub>2</sub>	TRIP thiol	0.1	1.3	0.4
3	PBu <sub>4</sub> OP(O)(O <sup>n</sup> Bu) <sub>2</sub>	TRIP thiol	<0.1	1.3	0.8
4	PBu <sub>4</sub> OP(O)(O <sup>n</sup> Bu) <sub>2</sub>	Thiophenol	<0.1	2.0	0.9
5	PBu <sub>4</sub> OP(O)(O <sup>n</sup> Bu) <sub>2</sub>	Pentafluorothiophenol	0	trace	0
6	PBu <sub>4</sub> OP(O)(O <sup>n</sup> Bu) <sub>2</sub>	3,4-Difluorothiophenol	<0.1	2.1	1.4
<b>Change from conditions 6</b>					
7	no Ir photocatalyst		0	0	0
8		no light	0	0	0
9		no phosphate base	0	0.2	0
10		no thiol H-atom donor	0	0.7	0

<sup>a</sup>All reactions were performed with 12 mg of native lignin. Yields were determined by HPLC analysis of the crude reaction mixtures relative to an internal standard.

Encouraged by these results, we next investigated the catalytic depolymerization of native lignin material derived from grand fir, which was extracted from the corresponding sawdust using a previously reported acidolysis procedure (See SI for details).<sup>14</sup> Blue light irradiation of 12 mg of fir lignin in dioxane for 24 h with the optimal catalysts from Scheme 1 resulted in the formation of an organic-soluble fraction together with an insoluble solid fraction. HPLC analysis of the soluble fraction revealed three major monomeric products, including 3,4-dimethoxybenzaldehyde (**M**<sub>1</sub>), vanillin (**M**<sub>2</sub>) and 4-(2-hydroxyethoxy)-3-methoxybenzaldehyde (**M**<sub>3</sub>), which were confirmed by comparison with authentic standards. The structures of **M**<sub>2</sub> and **M**<sub>3</sub> suggest that these products were formed *via* the C–C bond scission of consecutive  $\beta$ -O-4 linkages. Notably, monomers formed upon the cleavage of  $\beta$ -1 linkage were not detected, possibly due to the low percentage of this linkage in softwood lignin (1–9 wt%).<sup>4m</sup>

Under the optimal conditions for the fragmentation of model lignin dimers, grand fir lignin was depolymerized to provide three monomers in only 0.3 wt% each (Table 1, entry 1). Seeking to improve on these results, we investigated a number of phosphate bases and found that tetrabutylphosphonium di-*tert*-butylphosphate was the most efficient, improving the yields of **M**<sub>2</sub> and **M**<sub>3</sub> to 1.3 and 0.8 wt% respectively while minimizing the formation of **M**<sub>1</sub> (entries 2, 3). Evaluation of the reaction efficiency with different thiol co-catalysts revealed that 3,4-difluorothiophenol was optimal, providing **M**<sub>2</sub> and **M**<sub>3</sub> up to 2.1 and 1.4 wt% respectively while only <0.1 wt% of **M**<sub>1</sub> was obtained (entries 3–6). Control experiments revealed a complete loss of reactivity in the absence of either iridium photocatalyst or visible light irradiation (entries 7, 8). With no phosphate base or thiol, only trace quantities of **M**<sub>2</sub> (0.2 and 0.7 wt% respectively) were observed (entries 9, 10). In the reactions without phosphate, it is possible that arene radical cation-based fragmentation pathways may be operative, in line with previous studies by Mariano.<sup>8, 15</sup> In the reactions without thiol, the phenolic O–H bonds present in lignin itself may serve as H-atom donors. This hypothesis is consistent with control experiments in the absence of thiol, where phenolic dimer **2** fragments to provide **2a** and **1b** in 13% and 5% yield, respectively.

The total weight percentage of recovered monomers from the depolymerization process is not a precise measure of the efficiency of this depolymerization method, due to the fact that monomeric products are only liberated if two consecutive  $\beta$ -O-4 linkages are cleaved. Therefore, we also determined the proportion of  $\beta$ -aryl ether bonds cleaved herein as a percentage of the total cleavable  $\beta$ -aryl ether bond content of the sample, which was estimated as the molar ratio between the monomers obtained from our photocatalytic conditions, compared to the total cleavable  $\beta$ -aryl ether bonds in the substrate as determined by the established DFRC method (See SI for details).<sup>16</sup> This analysis suggests that at least 41% of the total  $\beta$ -aryl ether bonds in grand fir lignin were fragmented under our PCET conditions (Table 2, entry 1). It should be noted that this calculation represents a lower bound on the efficiency of our depolymerization method, as it neither takes into account the cleavage of nonconsecutive  $\beta$ -O-4 linkages, nor corrects for the actual number of  $\beta$ -O-4 linkages containing



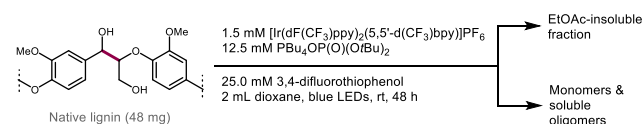
**Figure 2.** Catalytic depolymerization of native grand fir lignin. (a) HSQC analysis of native lignin prior to and after depolymerization. (b) GPC analysis of lignin prior to and after depolymerization.

a free benzylic O–H group, which is crucial for the PCET activation process.

We also investigated this depolymerization process *via* HSQC and GPC experiments. The HSQC analysis of the soluble fraction of the post-reaction mixture suggests a significant degree of depolymerization *via* rupture of the  $\beta$ -O-4 linkage, as the characteristic signals attributed to C<sub>α</sub>-H and C<sub>β</sub>-H as compared to the initial lignin were substantially diminished (Figure 2a). Furthermore, HSQC signals for a number of aldehyde products were also observed, consistent with the hypothesized C–C bond scission mechanism and suggesting the formation of various oligomeric aldehyde-containing fragments in addition to the quantified monomeric aldehyde products (Figure 2a). Moreover, gel permeation chromatography (GPC) measurements of the soluble fraction revealed a notable decrease in the molecular weight of the fragmented lignin as compared to the original polymer, as well as the appearance of lower-MW oligomeric and polymeric material (Figure 2b). MS analysis of the post-reaction mixture also suggested an increase in low-MW products following depolymerization compared with the original lignin sample (See SI). Interestingly, the examination of the insoluble fraction obtained from the post-reaction mixture *via* HSQC showed none of the characteristic signals corresponding to the aromatic moieties of the lignin polymer (Figure S16,17). This observation suggests that significant quantities of unidentified impurities may remain in the lignin sample following dioxosolv extraction.

We next sought to establish the stability of the monomeric products under the reaction conditions. After 24 h of irradiation of the pure monomeric products under the optimized conditions, we recovered 100%, 95% and 92% of **M**<sub>1</sub>, **M**<sub>2</sub> and **M**<sub>3</sub>, respectively. Interestingly, no conversion of **M**<sub>3</sub> to **M**<sub>1</sub> through further  $\beta$ -scission of the primary alcohol was observed in these stability studies, highlighting the excellent selectivity of this protocol for cleavage of the central C–C bond of the  $\beta$ -O-4 linkage.

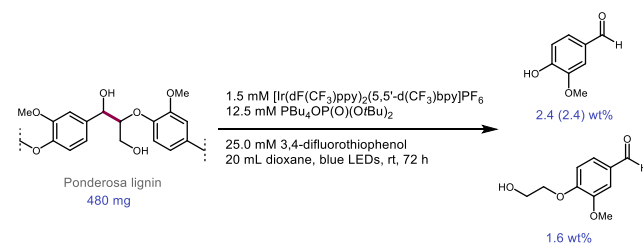
**Table 2.** Depolymerization of different lignin materials.<sup>a</sup>



Entry	Biomass	Insoluble fraction (wt%)	<b>M</b> <sub>1</sub> (wt%)	<b>M</b> <sub>2</sub> (wt%)	<b>M</b> <sub>3</sub> (wt%)	<b>M</b> <sub>2</sub> + <b>M</b> <sub>3</sub> (wt%)	$\beta$ -ether bond cleavage (%) <sup>b</sup>
1	Grand fir	44	<0.1	2.1	1.3	3.4	41
2	Ponderosa	50	<0.1	2.3	1.4	3.7	34
3	Cedar	33	<0.1	3.0	1.8	4.8	42
4	Larch	39	<0.1	3.2	1.9	5.1	22

<sup>a</sup>All reactions were performed with 48 mg of native lignin. Yields were determined by HPLC analysis of the crude reaction mixtures relative to an internal standard, and represent the average of two experiments. <sup>b</sup>Percentage of  $\beta$ -ether bond cleavage was calculated as the molar ratio of monomers obtained from our conditions as compared to the DFRC conditions (See SI for details).

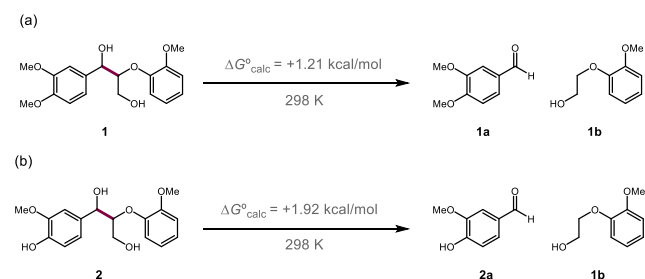
The depolymerization of lignin material derived from other plant species was also examined (Table 2, entries 2–4). Lignin samples obtained from ponderosa, cedar and larch sawdust were subjected to blue LED irradiation under the optimal catalytic conditions, resulting in depolymerization reactivity comparable to that of grand fir lignin. The amount of insoluble material following the reaction varied by species, with cedar releasing 33 wt% relative to the original weight of lignin samples, while ponderosa lignin produced 50 wt%. Moreover, cedar and larch lignin afforded higher total yields of monomeric products (up to 4.8 and 5.1 wt%, respectively) compared to the fir and ponderosa (3.4 and 3.7 wt%, respectively).



**Figure 3.** Preparative scale depolymerization reaction of ponderosa lignin. Assay yields were determined by HPLC analysis of the crude reaction mixtures relative to an internal standard. Yield reported in parentheses is for isolated and purified material.

We next demonstrated the feasibility of this depolymerization protocol on a preparative scale (Figure 3). Upon subjecting 480 mg of ponderosa lignin to the optimized reaction conditions, we were pleased to find that monomers **M**<sub>2</sub> and **M**<sub>3</sub> were formed in 2.4 and 1.6 wt% respectively, in close agreement to the yields obtained in the 48 mg scale reactions (Table 2, entry 2). Monomer **M**<sub>2</sub> was also isolated directly from the reaction mixture by silica gel chromatography (11.6 mg, 2.4 wt%).

A previous computational analysis of these light-driven  $\beta$ -scission reactions suggested that the products resulting from C–C bond cleavage are often higher in energy than the corresponding starting materials.<sup>10b</sup> While the exact thermochemistry associated with depolymerization of a structurally complex macromolecule is challenging to determine computationally, DFT analysis of the cleavage of the  $\beta$ -O-4 model systems **1** and **2** suggests that the redox-neutral C–C scission events here may also proceed in a formally endergonic fashion, where the photon absorption events serve to drive the reaction in opposition to a thermodynamic bias (Figure 4).<sup>17</sup>



**Figure 4.** Calculated fragmentation thermochemistry for lignin dimers (M06-2X/6-311G++(d,p)//M06-2X/6-31G(d)).

In conclusion, we have developed a mild, one-step, light-driven protocol for the redox-neutral depolymerization of native lignins. Despite of the presence of numerous chemically distinct hydroxyl groups in the polymer, this PCET-driven approach exhibits selectivity for cleavage of the central C–C bond of the  $\beta$ -O-4 linkage, providing a well-defined and isolable set of monomeric arene products. We are hopeful that these results will prompt further interest in both utilizing PCET methods to achieve selective lignin depolymerization, and applications in the depolymerization of other classes of macromolecules.

## ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website.

Experimental details, characterization data, spectral data, and computational results (PDF)

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## Notes

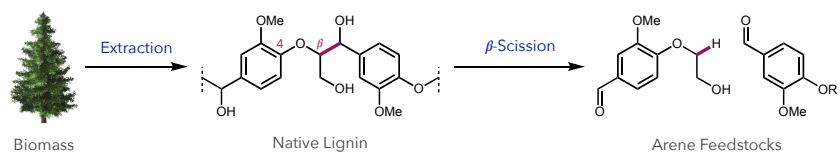
No competing financial interests have been declared.

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